

## *Recommendation for Conditional Approval of the PERACLEAN® Ocean Ballast Water Treatment System*

### Executive Summary

In order to eliminate one of the more common routes for the introduction of invasive species into state waters, RCW 77.120.030(2) forbids the discharge of unexchanged or untreated ballast water into waters of the state after July 1, 2007. WAC 220-77-095 describes the process for approval of ballast water treatment systems by the Washington Department of Fish and Wildlife (WDFW). Degussa has applied to WDFW for approval of the PERACLEAN® Ocean Ballast Water Treatment System (BWTS). The Washington Department of Ecology Water Quality Program (WQP) will be advising WDFW on environmental safety issues and setting conditions on the discharge of biocide-treated ballast water. WAC 220-77-095(2)(d)(v) provides the WQP with the criteria for this review: "The discharge from a technology must be environmentally sound and in compliance with existing water quality discharge laws."

The PERACLEAN® Ocean BWTS uses a mixture of 15% peracetic acid, 26.5% acetic acid, and 14.3% hydrogen peroxide ( $H_2O_2$ ) in order to destroy living organisms in ballast water. The remainder of the formulation is water and < 1% acid stabilizers. Treatment consists of dosing ballast water during intake to a concentration of 150 mg/L PERACLEAN® Ocean. The active toxicants at 150 mg/L are peracetic acid and hydrogen peroxide. These compounds decompose in ballast water and toxicity is expected to decline to a safe level before discharge. A study with PERACLEAN® Ocean in natural seawater from Kiel Harbor in Germany found over 90% reduction in peracetic acid and hydrogen peroxide within 24 hours.

The WQP required Degussa to toxicity test seawater treated with PERACLEAN® Ocean to determine conditions safe for discharge. Based on the results, the WQP predicts with confidence that a discharge of ballast water treated with PERACLEAN® Ocean will be environmentally safe as long as the conditions below are met. The WQP recommends that WDFW grant conditional approval for the use of the PERACLEAN® Ocean BWTS on one vessel to allow further evaluation of its effectiveness and environmental safety. Conditions for approval include the physical controls, time constraints, maximum concentrations, and further toxicity testing discussed below. Questions about the recommendation or conditions should be directed to Randall Marshall at [rmar461@ecy.wa.gov](mailto:rmar461@ecy.wa.gov) or 360-407-6445.

### Results of Toxicity Testing of Seawater Treated with PERACLEAN® Ocean

Toxicity tests assessed PERACLEAN® Ocean effects on survival and growth for silverside minnows (*Menidia beryllina*) and mysids (*Americamysis bahia*), survival and normal development for mussel (*Mytilus sp.*) and Pacific herring (*Clupea pallasii*) embryos, germination and germ tube length for giant kelp (*Macrocystis pyrifera*) zoospores, 96-hour population growth for diatoms (*Skeletonema costatum*), and 96-hour survival for Pacific herring larvae. The most sensitive test endpoint was mussel normal-survival with an  $EC_{50}$  of 3.6 mg/L PERACLEAN® Ocean. Herring embryo normal-hatch was the second most sensitive endpoint with an  $EC_{50}$  of 5.9 mg/L. Herring embryos were also tested with PERACLEAN® Ocean aged for 48 hours and toxicity was completely gone by then. However, a 48-hour aged PERACLEAN® Ocean solution still showed some toxicity to mussel embryos with an  $EC_{50}$  of 28 mg/L PERACLEAN® Ocean. A substance with toxicity to mussels was persisting in the test solution.

Analysis showed that measurable peracetic acid was gone within 7 hours after dosing at 150 mg/L PERACLEAN® Ocean, but that hydrogen peroxide remained at toxic concentrations for over 96 hours. Because hydrogen peroxide might be the only toxicant affecting mussels 48 hours after dosing, a test was conducted with  $H_2O_2$  by itself and the  $EC_{50}$  for mussel normal-survival was 1.6 mg/L. This  $EC_{50}$  is close to an  $EC_{50}$  (~2.7 mg/L) estimated by adjusting PERACLEAN® Ocean mussel test results to reflect  $H_2O_2$  measurements in aged PERACLEAN® Ocean solution indicating that hydrogen peroxide is the sole toxicant at 48 hours. An aged solution treated with an enzyme (catalase) used by living organisms to decompose  $H_2O_2$  lost all toxicity to mussels providing further verification. The persistence of the hydrogen peroxide in the lab is clearly due to the use of clean water lacking the metals and organics which would ordinarily catalyze the breakdown of  $H_2O_2$  in ballast water. The breakdown products are water and oxygen.

## Conclusion

The expectation when testing began was that PERACLEAN® Ocean toxicity would be gone within 48 hours after dosing. When this expectation was not met and hydrogen peroxide was found to be the cause, Degussa reduced hydrogen peroxide in the formulation from 24% to 14.3%. The recommendation for approval is only for the 14.3% formulation. Because hydrogen peroxide will decompose quicker in natural seawater in ballast tanks, onboard trials measuring H<sub>2</sub>O<sub>2</sub> may produce results predicting that the 24% hydrogen peroxide formulation is also acceptably safe. The 24% formulation might be more effective in destroying living organisms in ballast water. Hydrogen peroxide also has the ability to degrade polycyclic aromatic hydrocarbons (PAHs), pesticides, and sulfides in ballast water and sediment.

Hydrogen peroxide is the only toxicant from PERACLEAN® Ocean remaining after 7 hours. The EC<sub>50</sub> for the most sensitive test (mussel normal-survival) was 1.6 mg/L H<sub>2</sub>O<sub>2</sub>. No mussels lived at the test concentration of 2.5 mg/L H<sub>2</sub>O<sub>2</sub> while normal-survival was not significantly different from the control at 1.25 mg/L H<sub>2</sub>O<sub>2</sub>. Such a sharp threshold makes it easy to set a maximum discharge concentration so that toxicity disappears immediately in the receiving environment. Appendix H, *Establishing the Environmental Safety of Ballast Water Biocides*, of Ecology Publication No. WQ-R-95-80 contains the option of setting a maximum discharge concentration equal to twice the EC<sub>50</sub> when the toxic threshold is sharp. This option provides a hydrogen peroxide maximum discharge concentration of 3.2 mg/L (twice the EC<sub>50</sub> of 1.6 mg/L), and slightly more than 1:2 dilution in the receiving water would take hydrogen peroxide at this concentration below its toxic threshold. The hydrogen peroxide sold to the public as an antiseptic contains close to 9,000 times as much H<sub>2</sub>O<sub>2</sub> as does ballast water with 3.2 mg/L. Hydrogen peroxide is measurable at 3.2 mg/L under field conditions and this can be done onboard a vessel just prior to ballast discharge. Since it is possible that the increased decomposition of hydrogen peroxide in ballast water will bring its concentration below the detection limit before discharge, it is necessary that a solution of H<sub>2</sub>O<sub>2</sub> at around 3 mg/L in clean water be available to confirm the field method capability and detection limit.

## Approval Conditions

1. The PERACLEAN® Ocean concentration shall not be above 150 mg/L in newly treated ballast water.
2. The PERACLEAN® Ocean dosing pump shall be sized so that the maximum pumping rate will result in no more than 150 mg/L at the maximum ballast water intake rate.
3. The PERACLEAN® Ocean storage tank shall contain no more than the volume necessary to achieve 150 mg/L in the vessel's ballast water during one trial voyage and have secondary containment equal to its full volume.
4. Ballast water treated with no more than 150 mg/L of PERACLEAN® Ocean (14.3% H<sub>2</sub>O<sub>2</sub> formulation) may be discharged to state waters if at least 8 hours has elapsed since ballast water dosing and the hydrogen peroxide concentration is no more than 3.2 mg/L as measured by an analytical method demonstrated to have a low enough detection limit for this purpose.
5. Logs shall be kept of the operation of the BWTS and all of its controls, sensors, and alarms.
6. A flow-weighted composite sample from the full duration of the first discharge of the PERACLEAN® Ocean BWTS shall be tested for toxicity to silverside minnows (*Menidia beryllina* in EPA-821-R-02-014), a mysid (*Americamysis bahia* in EPA-821-R-02-014), mussel survival and development (*Mytilus* sp. in EPA/600/R-95-136), and giant kelp (*Macrocystis pyrifera* in EPA/600/R-95-136).
7. If Degussa wants to meet international recommendations, a 72-hour growth inhibition test with a marine diatom (*Skeletonema costatum* according to ISO 10253) may also be performed.
8. The most sensitive test from condition 6. above shall be conducted on each discharge event during the conditional approval period. If this test shows no toxicity at or below 50% sample in samples from 3 consecutive discharges of treated ballast water, then the lack of toxicity will be considered verified and toxicity testing may cease.
9. If any discharge occurs from the beginning of February until the beginning of June, a Pacific herring embryo survival and development test shall also be conducted. Contact Randall Marshall at [rmar461@ecy.wa.gov](mailto:rmar461@ecy.wa.gov) or 360-407-6445 for instructions on herring toxicity testing.